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Abstract

The impedance and electrical conductivity behavior of gellan gum hydrogels containing the conducting fillers poly(3,4- ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) and vapour grown carbon nanofibers (VGCNF) is presented. Impedance analysis showed that an equivalent circuit consisting of a Warburg element in series with a resistor could be used to model the gels' behavior. It is demonstrated that the addition of the conducting fillers PEDOT:PSS and VGCNFs can result in a measurable improvement in the conductivity of hydrogels with high water content and swelling ratios. Incorporation of combinations of these conducting fillers resulted in an improvement of the conductivity of gellan gum-containing hydrogels with water content (swelling ratio) of at least 97.5% (40) from 1.2 ± 0.1 mS/cm to 4 ± 0.6 mS/cm.

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Electrical conductivity and impedance behavior of hydrogels

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ABSTRACT

The impedance and electrical conductivity behavior of gellan gum hydrogels containing the conducting fillers poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) and vapour grown carbon nanofibers (VGCNF) is presented. Impedance analysis showed that an equivalent circuit consisting of a Warburg element in series with a resistor could be used to model the gels' behavior. It is demonstrated that the addition of the conducting fillers PEDOT:PSS and VGCNFs can result in a measurable improvement in the conductivity of hydrogels with high water content and swelling ratios. Incorporation of combinations of these conducting fillers resulted in an improvement of the conductivity of gellan gum-containing hydrogels with water content (swelling ratio) of at least 97.5% (40) from 1.2 ± 0.1 mS/cm to 4 ± 0.6 mS/cm.

Keywords: Hydrogel, Impedance, Electrical conductivity, Gellan gum, PEDOT, Carbon nanofibres, Conducting gels

1. INTRODUCTION

Hydrogels are highly swollen, materials prepared from hydrophilic polymers that can absorb up to a thousand times their dry weight in water. As a result of their high water content, most hydrogels are soft and weak materials compared to other polymeric materials such as rubbers. For this reason, hydrogels are typically utilized for applications that do not require them to be particularly strong or resilient (for example, in foods, ointments and creams). Soft-robotic applications require soft materials which are both electrically conducting and mechanically compliant[1]. Gels based on biopolymers are suitable candidates for such materials as they are classified as soft materials[2]. Conducting polymers are well-known materials, which can be used to fabricate conducting composites. For example, it has been found that conducting polymers have enhanced the lifetime of neural implants by reducing localized tissue damage[3]. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) is a block copolymer consisting of anionic PSS and cationic PEDOT. It is a conducting polymer which has been used in applications such as humidity and temperature sensors, anti-static coatings and actuators[4-6].

Vapour-grown carbon nanofibers (VGCNFs) are a conducting graphitized carbon filler material (first manufactured in 1889) which shares structural similarities with carbon nanotubes. VGCNF composite materials have been produced using a variety of polymeric fillers. For example, recently it was demonstrated that shape memory properties of VGCNF-epoxy composite materials were enhanced by chemical functionalisation of VGCNFs[7]. Other potential applications include their use in electromagnetic interference shielding materials.

Gellan gum is a linear anionic polysaccharide derived from the bacterium *Pseudomonas* (or *Sphingomonas*) *elodea* [8]. GG has been granted FDA (Food and Drug Administration) and EU (E418) approval for use in food[9] and currently has a wide range of applications due to its gel-forming characteristics [10]. Aside from these applications, it has also been shown to be an efficient dispersant of conducting carbon fillers [11-13], and previous studies have used it in conjunction with PEDOT:PSS to prepare electrically conducting composite hydrogels [14].

In this paper, we present the preparation and characterisation of conducting filler containing GG hydrogels. Combinations of the conducting fillers PEDOT:PSS and VGCNFs are incorporated into hydrogels using mixing and sonication, followed by physical cross-linking of the gellan gum network with Ca^{2+} ions. The gel's electrical behavior is characterized using impedance analysis which is used to evaluate the electrical conductivity.

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2. EXPERIMENTAL DETAILS

2.1 Preparation of dispersions

PEDOT:PSS (conductive grade, 13 mg/mL in water, batch no. MKBJ4242V) was purchased from Sigma Aldrich (Australia). Vapour grown carbon nanofibres (VGCNFs, PR24-LHT, Batch info: PS 1345 Box 8, HT 170) were purchased from Pyrograf Products Inc. (USA). Low-acyl gellan gum (GG) was received as a gift from CP Kelco (USA, Gelzan, Lot # 1I1443A). All solutions and subsequent gels were prepared with Milli-Q water (resistivity = 18.2 MΩ·cm). Gellan solutions were prepared by adding dry GG powder to heated (~80^{o}C) water under rapid stirring (800 r.p.m.) using an overhead stirrer (IKA RW 20 digital). Homogenous carbon nanofibre-gellan gum (FG) and carbon nanofibre-conducting polymer (PF) dispersions were prepared by adding various quantities of VGCNF powder to GG and PEDOT:PSS solutions, respectively. These were then sonicated using a digital sonicator horn (Branson Digital Sonifier) with a power output of 6 W in pulse mode (0.5 s on/off) and a tapered microtip (Consonic, diameter 3.175 mm) placed 1 cm from the bottom of a glass vial (diameter 25 mm), for up to 20 minutes.

2.2 Preparation of hydrogels

Cross-linked hydrogels were prepared with a GG concentration of 5 mg/mL. FG hydrogels were obtained by first dispersing the VGCNFs in GG solutions, followed by adding fresh GG powder to the dispersion with constant heating (~80 ^{o}C and stirring) until fully hydrated. These hot solutions were then cross-linked using hot $CaCl_2$ (~80 ^{o}C, 5mM final concentration). Conducting polymer-carbon nanofibre-gellan gum (PFG) hydrogels were prepared as follows. First, VGCNFs were dispersed in a PEDOT:PSS dispersion, which was then heated to ~80 ^{o}C under stirring. Then, resulting hot PF dispersions (15 mL, 80 ^{o}C) were then mixed with hot GG solutions (5 mL, 20 mg/mL concentration, 80 ^{o}C), followed by cross-linking with $CaCl_2$ (~80 ^{o}C, 5mM). The hot PFG dispersions were then poured into cylindrical shaped plastic moulds (10 mm height, 16 mm diameter) and allowed to cool under controlled ambient conditions (21 ^{o}C, 50 % relative humidity) until completely gelled.

The swelling ratio of our gels is defined as the ratio of wet mass over dry mass. Volume fractions were calculated from using PEDOT:PSS (0.8 g/cm^3), VGCNF (1.95 g/cm^3), GG (1.3 ± 0.03 g/cm^3) and water densities.

2.3 Impedance measurements

The impedance behaviour of dispersions and hydrogels were assessed as follows. First, dispersions were poured into plastic sample holders (acrylic 1 cm width, 1 cm height, 0.5 - 2.5 cm length) containing two pieces of reticulated vitreous carbon (RVC, ERG Aerospace, USA, 20 pores per inch). RVC was used in order to create a contact between the hard instrument electrodes and the soft hydrogel materials. A custom-designed instrument was used to measure electrical impedance for frequencies between 1 Hz and 100 kHz [15]. Briefly, an alternating current signal (1 V peak voltage) was applied using a waveform generator (Agilent U2761A) across a circuit consisting of a known resistor (10 kΩ) and the gel sample. The impedance was obtained by measuring the potential difference across the known resistor with an oscilloscope (Agilent U2701A). Electrical conductivity of gel samples was calculated using electrical impedance values at varying lengths.

2.4 Statistical treatment

The reported results are averages of the values obtained. Reported numerical errors and graphical error bars are given as ± 1 standard deviation (SD). Data and outliers were rejected either when instrumental error was known to have occurred, or if data failed a Q-test with a confidence interval ≥ 95%.

3. RESULTS AND DISCUSSION

3.1 Impedance behavior of hydrogels

Conducting hydrogels were prepared first dispersion VGCNFs in a PEDOT:PSS dispersion followed by addition of GG before cross-linking the GG network with Ca^{2+}. The electrical conductivity of the hydrogels is assessed using electrical impedance analysis with a custom-build instrument as described in our previous work[15]. In brief, conducting hydrogels with ionic charge carriers can be modelled as a Warburg diffusion element in series with a resistor. Figure 1A shows a

Bode plot of a typical hydrogel. The impedance magnitude ($|Z|$) decreases with increasing frequencies and become independent of frequency above 1 kHz.

The corresponding Nyquist plot (Figure 1B) displays a linear relation between the real (Z') and imaginary (Z'') components of the impedance. At the intercept with the x-axis, the impedance is purely real ($Z'' = 0$) and the Z' value represents a resistance. The slope in the Nyquist plot is ~1, suggesting a 45° constant phase shift between real and imaginary components of the impedance. This can also be recognised from a log-log version of the Bode plot, i.e. slope of -1/2 in the low frequency region (data not shown). This suggests that the hydrogel is behaving like a Warburg diffusion element (Z_W), in series with a resistor (R_I). Under this model, Z' and Z'' are inversely proportional to the square root of the frequency (ω),

$$Z' = R_I + \mu/\sqrt{\omega}, \quad (1)$$

$$Z'' = \mu/\sqrt{\omega}, \quad (2)$$

where μ is the Warburg coefficient. This dependence is unique to the Warburg impedance and is generally referred to as the Warburg plot (Figure 1C). A fit of this data to equations 1 and 2 revealed $R_I = 280 \pm 3\ \Omega$ and $\mu = 460 \pm 80\ \Omega \cdot s^{-1/2}$. R_I and μ can also be determined by equivalent circuit modelling (Figure 1A), which yielded similar values.

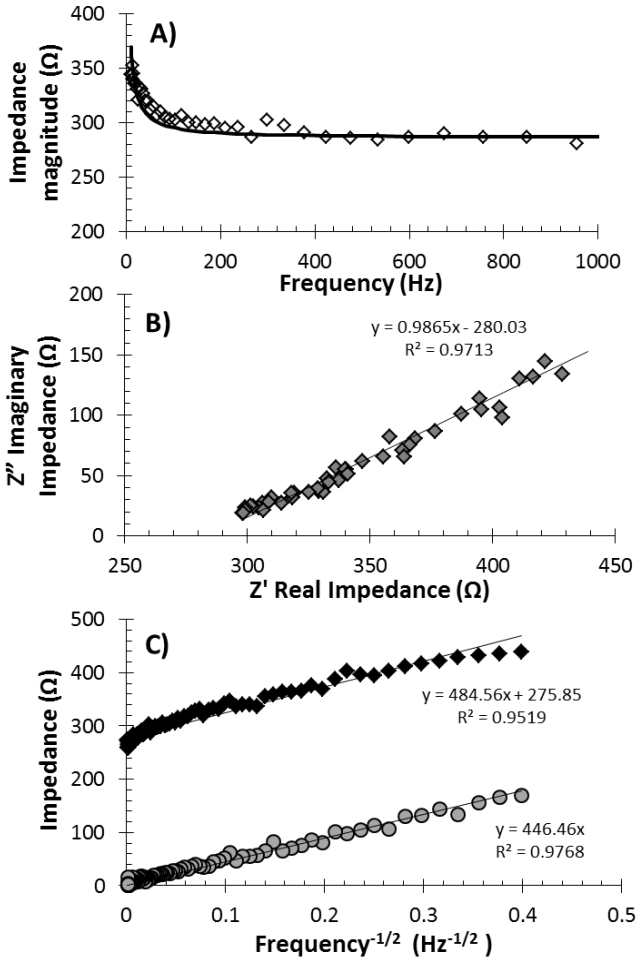

Figure 1. Electrical impedance analysis of a typical PEDOT:PSS-VGCNF-GG hydrogel (9.75 mg/mL PEDOT:PSS, 11.25 mg/mL VGCNF, 5 mg/mL GG) of dimensions 0.5 cm (l) x 1 cm (w) x 1 cm (h). A) Bode plot, B) Nyquist plot and C) Warburg plot. The solid line in A is a 2 parameter fit of data to an equivalent circuit model consisting of a Warburg element in series with a resistor, while the solid line in B is a straight line fit and C is a fit to equations 1 and 2.

The impedance values measured in this manner include a contact resistance, R_C, due to the interface between gel and electrodes (porous reticulated vitreous carbon, RVC). It was observed that the impedance magnitude (at any given frequency) increased with increasing gel length (data not shown).

In our previous work we demonstrated μ was invariant with length, while R_I was linearly proportional to gel length. This confirmed that the Warburg impedance is only significant at lower frequencies. Hence, the increase of R_I is directly related to the amount of gel material, which increases with length. This provided us with a method to correct the R_I value due to the presence of electrode-hydrogel contact resistance by realising that R_I vs l should obey,

$$R_I = l/(\sigma A_C) + R_C, \qquad (3)$$

where A_C is the gel's cross-sectional area and σ is the gel conductivity (at high frequencies). Fitting equation 3 to the data shown in Figure 2 yielded σ = 3.6 ± 0.3 mS/cm and a contact resistance value of 155 ± 30 Ω.

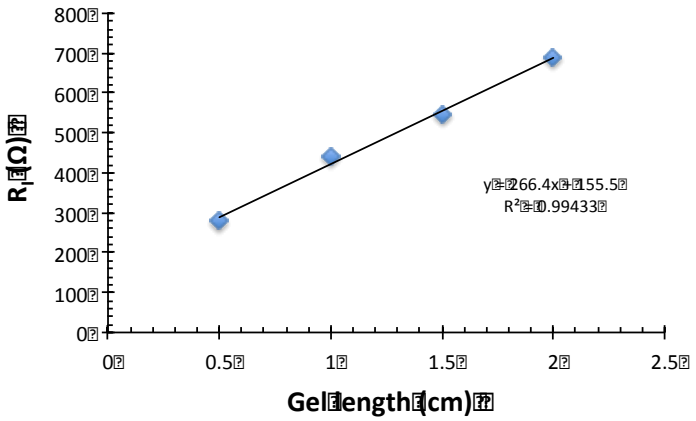

Figure 2. Gel electrical resistance values as a function of gel length for a typical PEDOT:PSS-VGCNF-gellan gum hydrogels as a function of VGCNF volume loading fraction. Solid line is a straight line fit to equation 3.

3.2 Conductivity behavior of hydrogels

Hydrogels consisting of gellan gum cross-linked with 5 mM Ca^{2+} exhibited conductivity values of 1.2 ± 0.1 mS/cm due to the presence of ionic charge carriers. Previously[14], we demonstrated that the conductivity of gellan gum hydrogels can be improved to 3.15 S/cm (a 2.6 fold increase) by incorporating PEDOT:PSS (water content and swelling ratio), see Figure 3A. In other work[15], we showed that addition of VGCNF to gellan gum improved the gellan gum conductivity to 2.0 S/cm (a 1.6 fold increase), see Figure 3B.

A comparison between the two different types of conducting gels reveals that at equivalent loading fractions and water content, PEDOT:PSS is clearly better then VGCNFs at enhancing the conductivity of gellan gum hydrogel.s For example, at volume fractions of approximately 0.8% the conductivity of a PEDOT:PSS containing gel is 3.15 mS/cm, whereas that of VGCNF containing gels is about 2 mS/cm. However, combining both fillers results in a further improvements as shown in Figure 3B. We found that the conductivity of gellan gum hydrogels could be improvement up to 4.0 ± 0.6 S/cm (a 3.3-fold increase compared to gellan gum gels).

In comparison, PEDOT:PSS composite hydrogels (water content 75-90%) exhibited values in the range 0.67 to 2.6 mS/cm depending on the conducting polymer content[16,17].

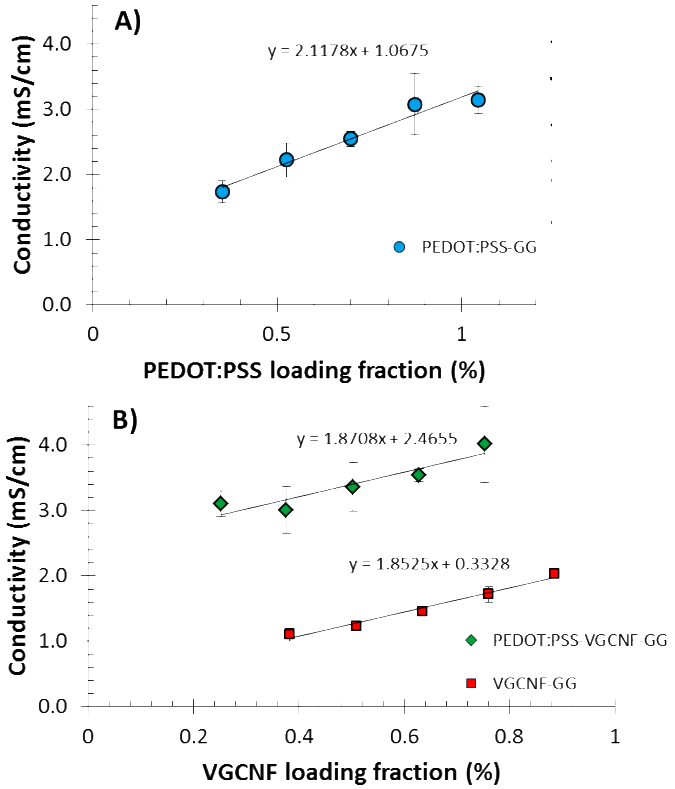

Figure 3. A) Electrical conductivity of PEDOT:PSS-gellan gum hydrogels (spheres, reproduced from reference 15) as a function of PEDOT:PSS volume loading fraction. B) Electrical conductivity of VGCNF-gellan gum (squares, reproduced from reference 14) and PEDOT:PSS-VGCNF-gellan gum (diamonds) hydrogels as a function of VGCNF volume loading fraction. All hydrogels are prepared with similar water content and swelling ratio (weight wet/weight dry) of 97.5 % (w/w) and 40 ± 2, respectively.

4. CONCLUSIONS

The impedance and conductivity characteristics of composite GG hydrogels containing PEDOT:PSS and carbon nanofibres are described. Hydrogel were prepared by dispersing VGCNF in a commercially available 1.3 % solution of PEDOT:PSS followed by addition of gellan gum. The electrical characteristics of these hydrogels were assessed using a custom-built impedance analyser. Our analysis revealed that the impedance behaviour of these gels could be modelled using a Warburg diffusion element in series with a resistor. These resistor values were used to calculate the conductivity after correcting for electrode-sample contact resistance.

Incorporating both PEDOT:PSS and VGCNF was found to result in an enhancement of the electrical conductivity beyond what can be achieved by either one of these conducting fillers on their. For example, incorporating either VGCNF or PEDOT:PSS results in maximum conductivity values of 2.0 mS/cm and 3.15 mS/cm, respectively. However, combining both fillers results in composite hydrogels (97.5% water content or swelling ratio of 40), which exhibited electrical conductivity values of up 4.0 ± 0.6 mS/cm.

The conductivity values of these gels (2-4 mS/cm) should be placed into the context of their water content and/or swelling ratio. It is well-known that the conductivity values will increase with a reduction in water content. Other researchers have reported similar and sometimes higher conductivity values for gels, but usually this is for gels which

contain less water and/or have a significantly lower swelling ratio. This paper contributes to the development of conducting hydrogel materials.

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